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PAPER

Easy fabrication of superporous zeolite templated carbon electrodes by electrospraying on rigid and flexible substrates

Juana M. Rosas, Ramiro Ruiz-Rosas, Raúl Berenguer, Diego Cazorla-Amorós,* Emilia Morallón, Hirotomo Nishihara, Takashi Kyotani, José Rodríguez-Mirasol* and Tomás Cordero

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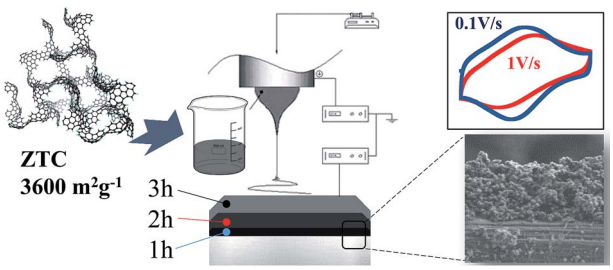

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Journal of Materials Chemistry A

PAPER

Easy fabrication of superporous zeolite templated carbon electrodes by electrospraying on rigid and flexible substrates†

Cite this: DOI: 10.1039/c6ta00241b

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Electrospraying of colloidal suspensions of superporous zeolite templated carbon (ZTC) nanoparticles in ethanol is herein proposed for the controlled deposition of continuous carbon coatings over different substrates, both rigid and flexible. By simple tuning of the concentration, feed rate, voltage and treatment time, different electrode thicknesses can be obtained avoiding the difficult manipulation of ZTC nanopowder formed by around 100 nm size particles. The addition of sulfonated tetrafluoropolyethylene (Nafion) in low amounts into the ZTC suspension improves the adhesion, increases the allowable surface loading and enhances the electrochemical performance of ZTC electrodes. ZTC/Nafion coatings from 0.1 to 1.5 mg cm^{-2} have been successfully arranged over graphite sheet and conductive carbon paper substrates. The obtained electrodes have been electrochemically characterized in 1 M H_2SO_4 electrolyte, demonstrating the unique and well-known pseudocapacitive features of ZTC, while showing capacitances as high as 700 mF cm^{-2} and outstanding rate performance thanks to the improved arrangement and connectivity of the ZTC nanoparticles. A supercapacitor using electrosprayed ZTC electrodes is constructed, showing specific capacitance higher than 60 F g^{-1}, capacitance retention of 63% when the current density is raised from 2.5 to 80 A g^{-1}, energy density of 6.6 W h kg^{-1} and maximum deliverable power greater than 240 kW kg^{-1}. These are promising results that make feasible the use of electrospraying for processing nanostructured carbon materials into electrodes of tunable thickness and deposited on substrates of different compositions and morphologies.

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1. Introduction

The last few decades have seen the blossoming of nanostructured carbon materials, in which sp^2 bonded carbon atoms exist in different dimensional arrangements forming nanosized particles. These materials have attracted the attention of the scientific community due to a number of highly valuable properties they possess. They have high electrical and thermal conductivities, unique electronic and optical properties, high chemical stability, large specific surface areas and good mechanical strength that enable them to be used in a growing number of established and novel applications. Specifically, nanostructured carbon materials can be used as electrodes in energy storage and conversion systems such as fuel cells and supercapacitors, where good electrical conductivity, high electrochemical stability, tunable surface chemistry and a large surface area are necessary.[1] Furthermore, nanostructured materials are well suited for miniaturized, portable or flexible devices,[2] in which the size and mechanical strength of the nanostructured materials are also relevant. In these applications, processability of the materials into thin films is of paramount importance, for which new techniques that could allow precise control of thickness and loading amount, and minimization of wasted material while preserving the outstanding performance of the carbon material are still necessary.[2]

Among the different nanostructured carbon materials zeolite-templated carbons (ZTCs) stand out. ZTC is an ordered microporous carbon comprised of an interconnected 3D buckybowl-like nanographene network. Its huge gravimetric (2000–4000 m^2 g^{-1}) and volumetric (1400–1700 m^2 cm^{-3})

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† Electronic supplementary information (ESI) available: Details about electrospraying on different substrates and in the absence of Nafion. See DOI: 10.1039/c6ta00241b

surface areas, three-dimensionally arrayed and mutually connected 1.2 nm pores and extremely large amount of edge sites,[3] susceptible to functionalization for pseudocapacitive-like reactions,[4] make ZTC a promising candidate for supercapacitors in both aqueous and organic electrolytes.[2,5,6] This is an application where they perform better than other nanostructured materials like carbon nanotubes or graphene thanks to the much larger specific surface area of ZTC, adequate electrolyte accessibility and high mass transfer rate. However, the low density and small particle size of this material hinder its processability into electrodes. Since it is obtained as a nanosized powder (between the 200 nm primary particle size and the 2000 nm secondary particle size), the manipulation of the material to prepare adequate electrodes including the binder and conductivity promoter is very difficult using the conventional methods used for activated carbons. Several approaches, such as the preparation of paste in the presence of a binder and a conductive promoter,[6] and the template-directed method,[7] have so far been developed to conform these materials into electrodes, but they have inherent limitations in the homogeneity of the electrode, control of the thickness of coating, handiness of the process and the overall conductivity of the electrode.

Electrospraying and electrospinning techniques rely on electrostatic forces to expel micrometer sized droplets from a charged liquid. The conducting liquid is slowly injected through an electrified capillary tube and, under ideal conditions, the applied electric field causes the liquid to emerge from the nozzle in the shape of a cone, called the Taylor cone. The high electric field concentrated at the tip of the cone induces the ejection of a fine spray of charged droplets. If the liquid is a solution or suspension and sufficient solvent evaporation occurs as the droplets are accelerated towards the grounded substrate, the resulting charge concentration induces break-up of the droplet and the ultimate deposition of sub-micron to nanoscale particles on the substrate.[8,9]

Electrospraying of single or multiwall carbon nanotubes has already been reported, but it requires the use of additives as stabilizers, such as polyvinylpyrrolidone.[10] On the other hand, this technique has also been proposed to fabricate carbon black (CB), multiwall carbon nanotubes, and graphite black coatings for pyroelectric detectors, solar cells, supercapacitor electrodes and other related energy storage devices.[11–15] Furthermore, suspensions of activated carbon powder with size under 30 μm and several binders (PTFE, PVDF, methyl cellulose…) have been electrosprayed over aluminum or copper foils in order to prepare energy storage electrodes, although their electrochemical performance has not been reported.[16] However, the procedure required a curing stage at temperatures as high as 450 °C, which is not suitable for carbon materials whose structure is sensitive to high temperatures. Therefore, to the best of our knowledge, this technique has not been previously used to deposit superporous nanostructured carbon materials, such as ZTC. Therefore, the aim of this work is the use of electrospraying to deposit ZTC in the form of coatings with different thicknesses over different surfaces and thus, to demonstrate the feasibility of the method for a simple and straightforward preparation of high quality coatings that can be applied for both rigid and flexible substrates. The electrochemical behavior of the obtained electrodes has been evaluated in an aqueous-based electrolyte, 1 M H_2SO_4, in order to assess the capacitance, rate performance, energy and power densities, and cyclability of the electrosprayed electrodes.

2. Experimental section

2.1. Preparation of the nanostructured material

The ZTC nanostructured carbon material was prepared using a hard template synthesis reported elsewhere.[3,4] Briefly, a Y-zeolite/poly(furfuryl alcohol) (PFA) composite was heat-treated up to 700 °C, followed by carbon deposition from propylene (7% in N_2) at 700 °C for 2 h and heat treatment at 900 °C. The composite obtained was washed with HF (47% aqueous solution), and the resulting carbon was washed with abundant distilled water and air-dried at 120 °C overnight. Detailed structural and porous texture characterizations are included in Fig. 1S and 2S in the ESI.†

2.2. Electrospraying set-up

Electrospraying of ZTC suspensions was carried out in a home-made device presented in Fig. 1. It consisted of two syringe pumps (KD Scientific) equipped with 5 mL syringes (BD), a spinneret with two stainless steel coaxial needles and two high voltage DC power supplies (Glassman High Voltage, Series EL) that were connected to the metallic needle and the collector and oppositely polarized in order to generate the electric field required for the process. ZTC/Nafion suspensions were prepared by the addition of a controlled volume of a Nafion suspension (5 wt% in lower aliphatic alcohols and water, Sigma-Aldrich) to a ZTC suspension in ethanol (2.0 mg mL^{-1}), in order to achieve ZTC to Nafion weight ratios between 1 : 1 and 1 : 10. For the objectives of this work, the optimum amount of ZTC to Nafion was found to be 1 : 10.

The weight of ZTC or ZTC/Nafion mixture that was collected over the substrate was determined by drying the electrode under vacuum at 70 °C for 2 h and weighting the dried electrode using a microbalance (Kern ABS 220-4N and Sartorius ME Micro Balance ME36S models). The difference between the initial weight of the substrate and the weight of the dried electrode was considered to be the amount of ZTC or ZTC/Nafion mixture collected over the substrate.

Electrospraying was carried out targeting four different surfaces that were used as current collectors by directly connecting them to a positively polarized high voltage power supply (see the ESI† for more information). Between these substrates, a thin graphite sheet (DFP-1, 0.5 mm width, POCO graphite), labelled as PGT, and flexible conductive Toray paper (TGP-H-030, Toray), referred to as TGP, were further utilized for the preparation of ZTC electrodes for electrochemical characterization. These electrodes were prepared using the ZTC/Nafion suspension (2.0 mg mL^{-1} of ZTC, Nafion to ZTC ratio of 1 : 10) at a feed rate of 1.0 mL h^{-1}, and different thicknesses or surface

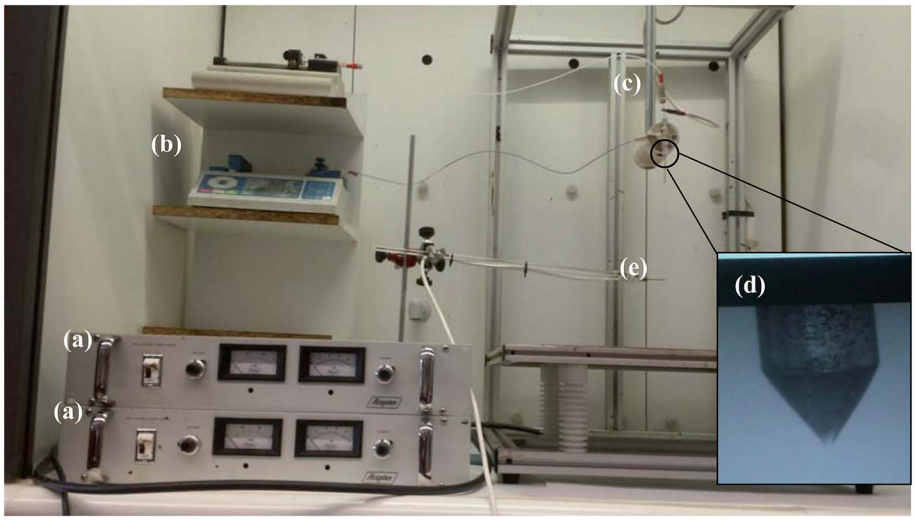

Fig. 1 Scheme of the electrospraying set-up. (a) High voltage power supplies with inversed polarization. (b) Syringe pump loaded with ZTC suspension. (c) Coaxial spinneret. (d) Details of the Taylor cone at the tip of the spinneret. (e) Substrate used as the current collector.

loadings of ZTC were obtained by modifying the time of electrospraying. A voltage of 10 kV and a tip-to-collector distance of 10 cm were applied for the synthesis of the electrodes. One PGT electrode was prepared in the absence of Nafion in the ZTC suspension (coaxial electrospinning, 0.5 mg mL^{-1} ZTC in ethanol feed at a constant rate of 1 mL h^{-1} through the inner needle, and 0.5 mL h^{-1} of pure ethanol through the outer needle), for comparison purposes.

2.3. Electrochemical characterization

Electrochemical characterization of the materials was carried out by using 1 M H_2SO_4 at room temperature in a T-type

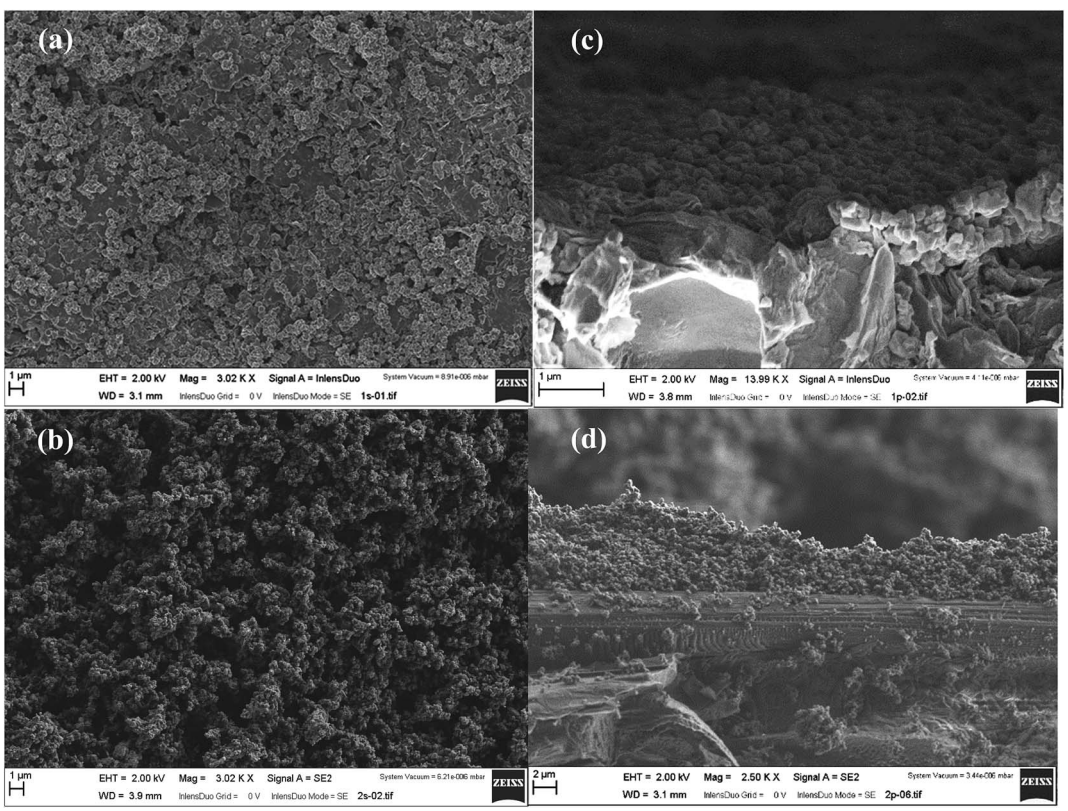

Fig. 2 FE-SEM images from the PGT graphite plate electrosprayed with ZTC/Nafion suspension, surface loading of ZTC: 0.11 mg cm^{-2}. (a and c) FE-SEM images from the TGP carbon conductive paper electrosprayed with the same suspension, surface loading of ZTC: 0.80 mg cm^{-2} (b and d).

Swagelok electrode cell equipped with a gold collector (surface: 0.196 cm^2). ZTC coatings supported on different surfaces and collectors were used as the working electrode, whereas a capacitive counter electrode made of activated carbon fiber and a much higher loading than the working electrode was used, which avoided the occurrence of undesired electrolyte decomposition. Both electrodes were vacuum dried at 80 °C overnight before the cell construction. An Ag/AgCl 3.0 M KCl electrode was used as the reference electrode. The working and counter electrodes were tightly pressed together while placing between them a nylon membrane (0.45 μm, Millipore) as a separator, and placed over the gold collectors and wetted with the sulphuric acid electrolyte for one day prior to the electrochemical measurements. The characterization of the capacitors was performed in two-electrode cells, and they were constructed with the electrosprayed ZTC on a carbon paper collector (Toray paper TGP-H-030) following the same protocol previously described for the 3-electrode measurements. The electrodes consisted of the carbon paper electrosprayed with a ZTC loading of 0.5 mg cm^{-2}, which were placed inside a two-electrode Swagelok cell equipped with stainless steel collectors (surface: 0.196 cm^2). Cyclic voltammetry and galvanostatic charge–discharge experiments were carried out in a VSP potentiostat (Biologic) using different scan rates (from 1 to 10 000 mV s^{-1}) and currents (from 0.2 to 32 mA).

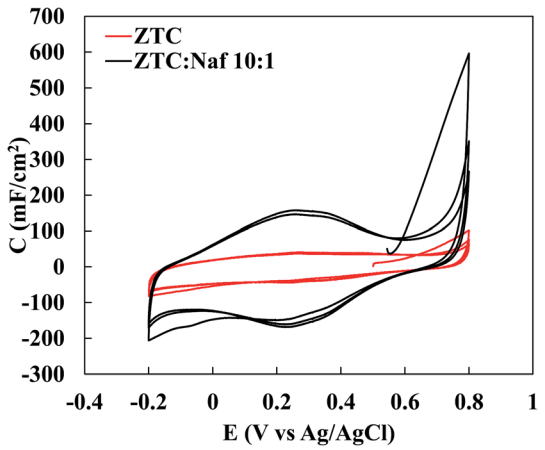

Fig. 3 Three-electrode cyclic voltammograms of PGT substrates coated with 0.21 mg cm^{-2} of ZTC, in the presence (black line) and absence (red line) of a binder. Scan rate: 5 mV s^{-1}.

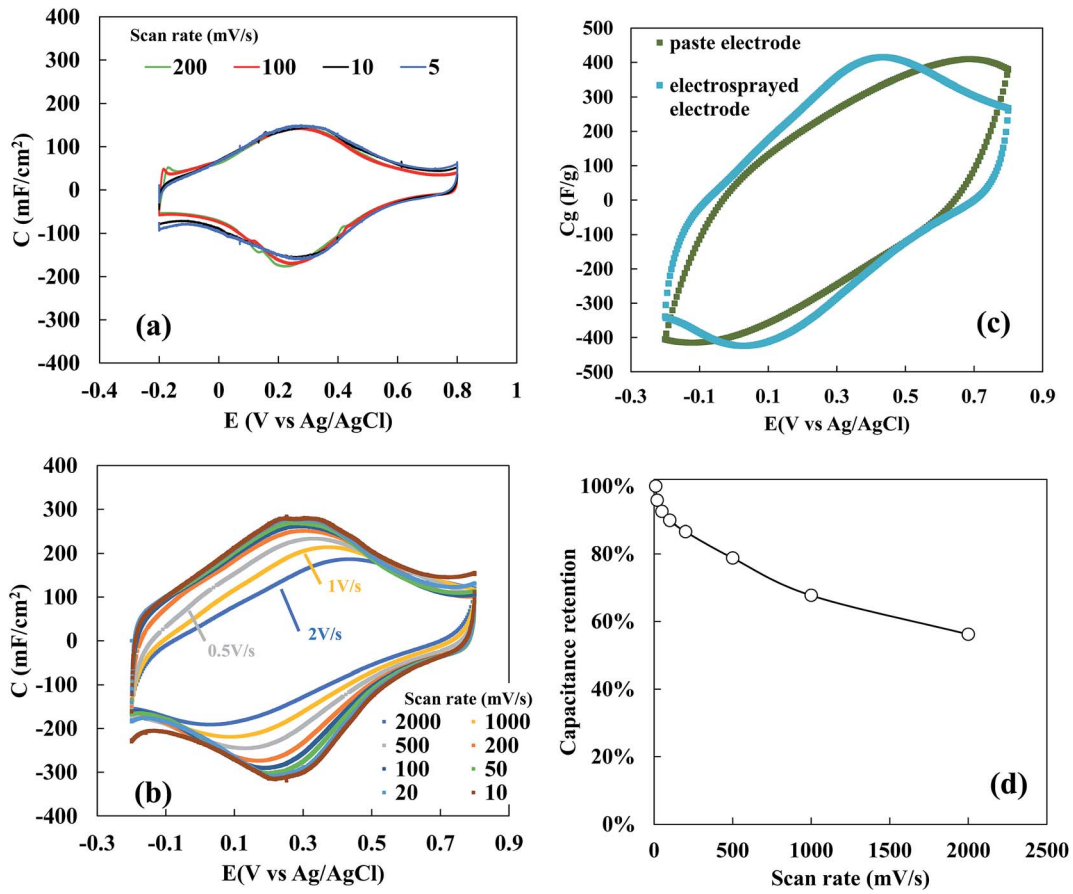

Fig. 4 Steady state cyclic voltammograms of ZTC/Nafion 10 : 1 coatings on the top of two different substrates. (a) PGT (0.2 mg cm^{-2}). (b) TGP (0.5 mg cm^{-2}). (c) Comparison between the cyclic voltammograms of a conventional ZTC paste electrode (90% ZTC, 5% acetylene black, 5% PTFE, 1.8 mg cm^{-2}) and ZTC/Nafion electrosprayed electrode over the TGP substrate (0.5 mg cm^{-2}). Scan rate: 2 V s^{-1}. (d) Capacitance retention *vs.* scan rate for TGP loaded with 0.5 mg cm^{-2} ZTC.

3. Results and discussion

3.1. Preparation of the electrodes

Electrospraying of ZTC suspension was performed over several different substrates (see the ESI†). It allowed us to demonstrate that coatings of powder ZTC could be achieved over any of the studied substrates, and the amount of ZTC was related to the time of electrospraying, although the adhesion of ZTC nanoparticles was poor and the amount of ZTC loaded on the substrate was limited by the low stability of the suspension, which stopped the process of electrospraying for more than an hour. The addition of Nafion solution in the ZTC suspension in a 1 : 10 Nafion to ZTC weight ratio was sufficient to provide better homogeneity of the suspension, which allowed us to use a ZTC loading in the suspension of 2.0 mg mL^{-1}, and also resulted in enhancement of the contact between the surface of the collectors and the ZTC/Nafion films, which, when wetted with 1 M H_2SO_4, did not show any loss of carbonaceous material to the electrolyte.

Fig. 2 shows FE-SEM images of the surface and the edge of graphite sheet and carbon paper substrates that have been electrosprayed with ZTC/Nafion for different loadings, respectively. In the case of low surface loading applied over the graphite substrate, the ZTC coating leaves some uncovered areas, where the graphite flakes that form the surface of the sheet can still be seen (Fig. 2a). Nevertheless, the image detailing the edge of the electrode revealed that the ZTC coating has an average thickness of *ca.* 1 μm (Fig. 2c). On the other hand, the higher surface loading displayed on top of the TGP surface produces a much more massive coating (Fig. 2b). The study of the edge of this electrode showed a thick ZTC coating over the carbon fibers that form the TGP substrate, with an average thickness of *ca.* 11 μm (Fig. 2d). Therefore, using the ZTC/Nafion suspension ZTC surface loadings as high as 1.5 mg cm^{-2} and good cohesion between the components of the electrode have been achieved over the conductive carbon paper and the graphite sheet.

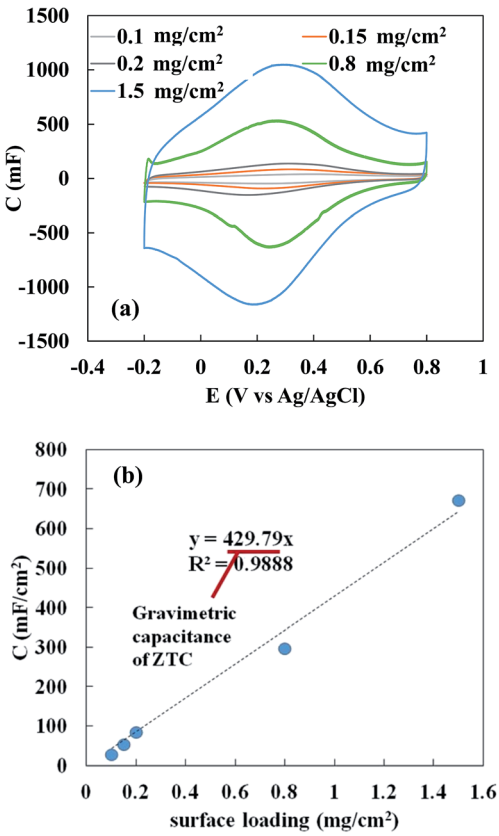

Fig. 5 (a) Steady state cyclic voltammograms of the PGT substrate coated with different amounts of ZTC/Nafion; (b) capacitance as a function of ZTC surface loading on the PGT substrate.

3.2. Electrochemical characterization of ZTC electrosprayed substrates

The electrodes prepared over TGP and PGT substrates were electrochemically characterized in 1 M H_2SO_4 in order to evaluate the effectiveness of the proposed methodology in the development of electrodes for energy storage. Firstly, the effect of the addition of Nafion during the formulation of the ZTC electrode on its electrochemical performance was assessed in a PGT graphite sheet that contained in both cases 0.2 mg cm^{-2} of ZTC (ZTC and ZTC/Nafion concentration: 0.5 and 2 mg mL^{-1}, respectively; injection flow rate: 1 mL h^{-1}; electrospraying times were adjusted to obtain a similar loading) and differed only in the presence of the binder in a 10 (ZTC) : 1 (binder) ratio in one of the samples (Fig. 3). As can be seen, the cyclic voltammogram of the electrode containing only ZTC shows a remarkably lower current than the sample containing Nafion, pointing out that the loose connectivity between ZTC particles and the collector is translated into poor electrical conductivity. The calculated gravimetric capacitance (105 F g^{-1}) is also much lower than that previously found for ZTC as a supercapacitor electrode in sulphuric acid electrolyte,[4,6] which may be indicative of a large part of the ZTC particles (more than 70%) electrosprayed over the collector being lost to the solution or unconnected to the current collector. In contrast, the voltammogram of ZTC using Nafion as the binder shows a much larger capacitance (97 mF cm^{-2} and 460 F g^{-1}) and the redox processes occurring at around 0.35 V (*vs.* Ag/AgCl/Cl^-(sat.)) characteristic of the electroactive quinone surface groups,[17] are clearly observed, these peaks being a well-known electrochemical fingerprint of this carbon material.[4] The formation of these surface oxygen groups is favored in sulfuric acid through a direct electro-oxidation mechanism that entails the polarization of the ZTC particles,[18] which suggests a low interparticle resistance in this electrode. On the other hand, the electrochemical characterization also suggests that the experimental conditions employed for obtaining a homogeneous suspension and electrospraying of the sample, such as the sonication of ZTC in ethanol and subjecting the suspension to a high voltage, do not damage the ZTC structure and surface properties.

Since the addition of a binder seems to be mandatory to achieve full performance of the ZTC coating, all the electrodes submitted to electrochemical characterization were prepared from a ZTC/Nafion solution using a 10 : 1 weight ratio.

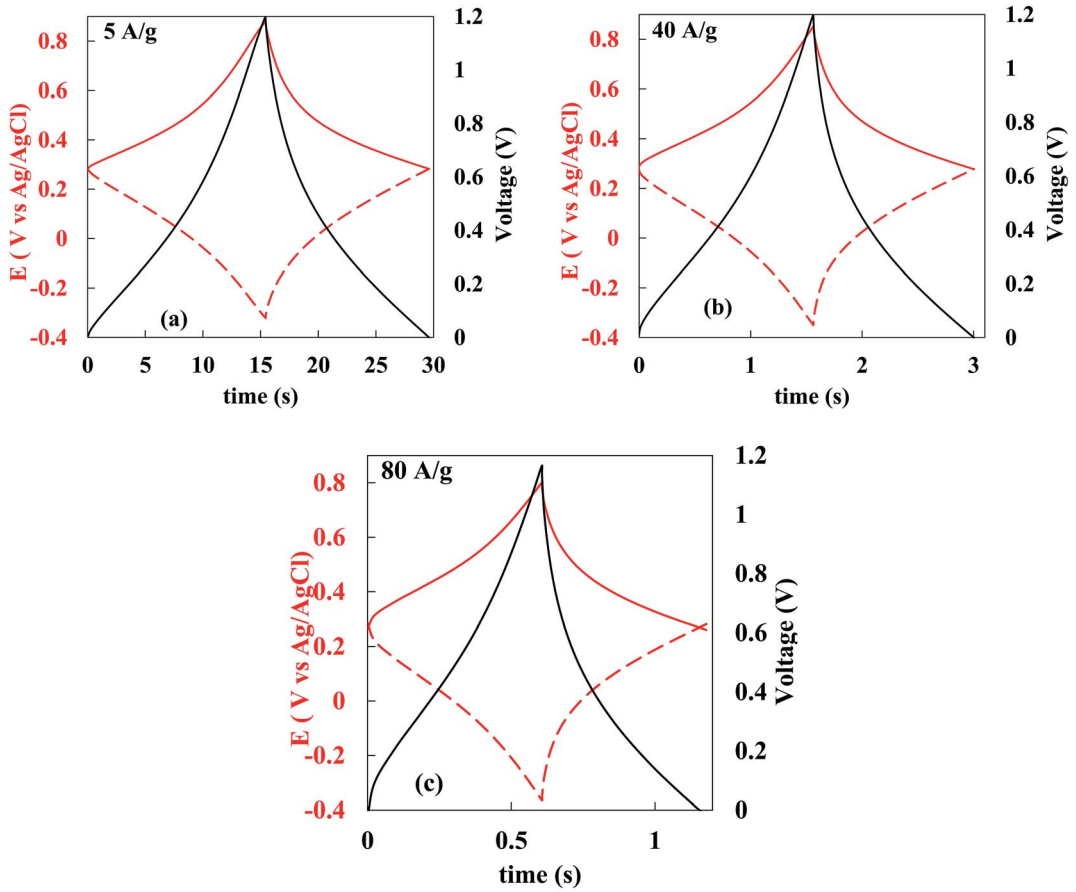

Fig. 6 Galvanostatic charge discharge profiles of a T-type 2-electrode cell constructed with ZTC/Nafion coated TGP electrodes (surface loading: 0.5 mg cm^{-2}). Cut-off voltage: 1.2 V, specific currents: (a) 5 A g^{-1}, (b) 40 A g^{-1} and (c) 80 A g^{-1}.

Fig. 4 shows the cyclic voltammograms at different scan rates for electrodes obtained with different amounts of ZTC deposited on different carbon collectors. The evaluated substrates in these experiments were the macroporous graphite sheet (PGT, Fig. 4a), and the conductive carbon paper (TGP, Fig. 4b–d), which is used as the gas diffusion layer of fuel cell electrodes. In all cases, the use of this technique allowed reproduction of the electrochemical behaviour of ZTC. Large capacitance retention and pseudocapacitive contribution were found even when the scan rate was increased to 2000 mV s^{-1} (Fig. 4b), confirming the extraordinary rate performance obtained using this technique. Surprisingly, the appearance of redox peaks related to the electrochemical behaviour of ZTC could still be observed even at a very high scan rate of 2000 mV s^{-1}, a feature that indicates the extraordinary interparticle connectivity achieved by this electrode, which offers ultra-high power handling capability. For comparison purposes, a ZTC electrode was prepared following a previously developed method which involved the use of polytetrafluoroethylene (PTFE) as the binder and acetylene black as a conductivity promoter, using a formulation of 90/5/5, respectively, and in dry conditions since addition of a solvent did not allow us to obtain a homogeneous paste.[4–6] We tried to prepare an electrode with a similar surface loading to that achieved by electrospraying, and it is important to note the inherent difficulty in preparing such thin film ZTC electrodes following the previously reported procedure. In fact, it was not possible to achieve well-formed electrodes with a surface loading lower than 1.8 mg cm^{-2} through this technique. The electrode with a surface loading of 1.8 mg cm^{-2} was electrochemically characterized by CV using the same procedure and the same cell described in the Experimental section for comparison purposes (Fig. 4c). It can be seen that, although the electrosprayed and the conventional paste electrodes showed similar capacitance values, the irreversibility of the redox process is much higher for the paste electrode, pointing out that, beyond the advantage of providing an easier procedure for the preparation of thin film ZTC electrodes, better conductivity is achieved through this method.

The loss of capacitance when the scan rate is increased in the ZTC/Nafion electrosprayed electrode from 5 to 200 mV s^{-1} is *ca.* 12%, and about 40% at a scan rate of 2000 mV s^{-1} (Fig. 4d). The results demonstrate that this technique is highly versatile from the point of view of its full compatibility with any conductive surface for the preparation of films of nanostructured carbon materials. It can also be seen that capacitance is clearly related to surface loading (Fig. 4a and b). The gravimetric capacitances for the PGT and TGP electrodes are 431 and 433 F g^{-1} at 10 mV s^{-1}, pointing out that, in spite of the different amounts loaded

on both substrates, all the electrosprayed ZTC particles over them are connected and available for storing charge. The scan rate was further increased in the case of the TGP electrode prepared with higher ZTC loading (Fig. 4d). The capacitance retention surpasses that obtained with electro-oxidized ZTC electrodes prepared using conventional processing methods,[6] which indicates that this method allows the achievement of better interparticle contact that can be used for processing electrodes with high power specifications. It is also noteworthy that this outstanding rate performance has also been achieved while avoiding the use of a conductive promoter (like carbon black).

On the other hand, the effect of ZTC loading (*i.e.* electrode thickness) on the rate performance of the electrode was also evaluated using the PGT substrate after electrospraying at different times with the same ZTC : Nafion suspension. Thus, the cyclic voltammograms recorded at a scan rate of 100 mV s^{-1} over the PGT with different ZTC loadings are shown in Fig. 5a. It can be clearly observed that the capacitance values measured from the voltammogram increase with the ZTC loading, being clearly sensitive to the amount of ZTC on the electrode. Fig. 5b shows the plot of capacitance as a function of surface loading. A linear relationship between capacitance and surface loading is observed. From the slope of this relationship a gravimetric capacitance value of 430 F g^{-1} is obtained. This value is close to that reported for ZTC electrodes in the same electrode,[4,6] constituting a very promising result, since it proves that, no matter what the amount of ZTC loaded over the top of the collector is, all ZTC particles are effectively connected to the current collector, yielding the full profit in the constructed electrode of the exceptionally high capacitance value of ZTC. Therefore, electrospraying of ZTC/Nafion suspensions can be employed for processing ZTC into electrodes of controllable thickness that could be employed in a wide range of applications, making it possible to achieve loadings closer to those of commercial capacitors, while avoiding the use of conductivity promoter additives and harsh treatments that could compromise the outstanding properties of ZTC.

3.3. Two-electrode cell characterization

The performance of capacitors at high charge–discharge current densities is also crucial for their practical application as energy-storage devices. Fig. 6 shows the galvanostatic charge discharge behavior of a capacitor which was constructed employing ZTC/Nafion electrodes wetted with 1 M H_2SO_4 and deposited on the top of Toray carbon paper (TGP, surface loading: 0.5 mg cm^{-2}), over a voltage of 1.2 V and by using different current densities. The potential values corresponding to the positive and negative electrodes *vs.* Ag/AgCl/Cl^-(sat.) (right *Y*-axis) during the galvanostatic charge–discharge experiment are also included in the figure.

Both the charge and discharge curves exhibit slight deviations from a straight and symmetric triangular profile, a typical feature of electrodes with voltage-dependent capacitance owing to the large pseudocapacitive contribution. From the observation of the transition between the charge and discharge curves,

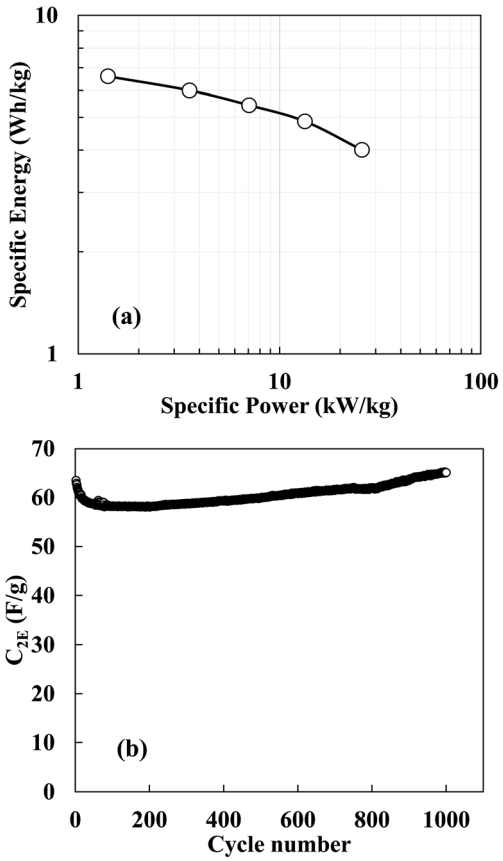

Fig. 7 (a) Ragone plot of a T-type 2-electrode cell constructed with ZTC/Nafion coated TGP electrodes (surface loading: 0.5 mg cm^{-2}). (b) Electrochemical stability under successive cycling at current densities of 5 A g^{-1} at 1.2 V.

it can be seen that a negligible ohmic drop is found even at the highest specific current tested, confirming the outstanding power characteristics of these electrodes. From the electrode potential curves (red lines), it can be seen that both electrodes work in symmetric potential windows at the three specific currents, always being within the previously reported stability limits of ZTC electrodes.[6] The two-electrode capacitance as a function of the specific current has also been determined. As expected, the effective capacitance value dropped upon application of increasing current densities, showing a capacitance of *ca.* 60 F g^{-1} at the lowest specific current and of 38 F g^{-1} at 80 A g^{-1}. Therefore, the loss of capacitance is only about 35% when increasing the specific current from 2.5 to 80 A g^{-1}. This result is also very similar to that obtained with a binderless ZTC thin film prepared through a much more time consuming procedure involving the electrophoretic deposition of zeolite nanoparticles.[7]

The values of specific power (*P*) and specific energy (*E*) were integrated from the area under the discharge curves and are presented in a Ragone plot, as shown in Fig. 7a. It displays a typical specific power–energy relationship, with a specific energy that remains almost unchanged at a low specific power and then gradually decreases when a higher power is demanded to the cell. An energy density value of 6.6 W h kg^{-1} is estimated

at the lowest power density (1.4 kW kg^{-1}), whereas at 25.7 kW kg^{-1}, the stored energy density by the 2-electrode cell is 4.0 W h kg^{-1}, which is delivered in only less than 0.5 seconds. From the ohmic drop determined at the highest specific current, the electrical series resistance (ESR) of the cell was estimated to be 6.3 mΩ, a value that in turn rendered a maximum deliverable power of 288 kW kg^{-1}, which was calculated using the widely accepted expression $P_{max} = V^2/4ESRm$, where V is the voltage of the cell, ESR is the electrical series resistance and m is the total mass of the two electrodes. This value is much higher than those obtained for ZTC symmetric cells,[6] although it should be noted that the smaller electrode thickness employed in this work could partially explain such a huge difference. Since this technique can be used to make a controlled deposition of the nanostructured carbon material with the desired thickness, it opens a variety of applications from supercapacitors to micro-supercapacitors that can harvest mechanical energy generated by piezoelectric nanogenerators, and then store the generated electric energy[19,20] or for the preparation of flexible supercapacitors.[2]

The electrochemical stability of the deposited layers was also investigated by performing 1000 charge–discharge cycles at 5 mA cm^{-2} over a voltage of 1.2 V. The capacitance retention during the durability test is shown in Fig. 7b. The value of capacitance even slightly increases after 1000 cycles probably due to better electrolyte impregnation with time and/or to the introduction of some oxygen electroactive functionalities, by electrooxidation, of ZTC upon successive cycling, increasing the pseudocapacitance contribution of the electrodes. This relevant result points out that the supercapacitor mounted using electrosprayed ZTC electrodes is able to safely operate at 1.2 V without any decrease in its performance.

4. Conclusions

A method based on the electrospraying technique for the controlled deposition of continuous films of a superporous zeolite templated carbon material over different current collectors, including both rigid and flexible substrates, is proposed. This technique is very selective, versatile and the experimental set-up is very simple. ZTC films can be easily prepared by electrospray deposition through a straightforward method which includes the addition of small amounts of Nafion as a binder and stabilizing agent in the spraying solution and without using any conductivity promoter. Furthermore, this technique can also be used in the preparation of ZTC thin films on very different supports. Loadings as low as 0.1 mg cm^{-2} (like those intended for microcapacitors, fuel cell electrodes, electrochemical biosensors and other electrical microdevices) and as high as 1.5 mg cm^{-2} (close to those used for commercial capacitors) can be reached, proving the flexibility of this technique. The rate performance of ZTC film electrodes prepared with this technique is better than that obtained from pastes using powder ZTC and similar to those of binderless ZTC films with lower loadings. The viability of this technique in the preparation of supercapacitor electrodes has been evaluated by constructing a 2-electrode cell with conductive carbon paper coated with 0.5 mg cm^{-2} of ZTC. The outstanding power characteristics of the resulting cell have been manifested by the excellent capacitance retention of 65% when the specific current is increased from 2.5 to 80 A g^{-1}. An energy density of 6.6 W h kg^{-1}, with a maximum power density higher than 240 kW kg^{-1} has been measured for the cell, this power value being much higher than those achieved with the conventional processing methods when applied to ZTC electrodes.

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